MicroEXAFS study into the oxidation states of copper coloured Hispano–Moresque lustre decorations

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Introduction

Lustreware is a traditional decorative finish applied to ceramics, giving a copper–gold metallic finish. Following an Islamic tradition, it was a highly prized luxury finish that was exported throughout the Mediterranean in medieval times. The technology required to produce the highly desired artifacts was the province of highly skilled artisans, that it was also non-trivial is evidenced by the slow development of rival production centres elsewhere and the large proportion of fragments from failed production runs found at the established centres.

Archaeometry is a comparatively new branch of archaeology which uses modern material science techniques, such as EXAFS, to determine the materials and technologies employed by early artisans. This in turn will give a clearer insight into the nature of historical economies and the societies they supported.

The goal of this project is to identify the local chemistry in the glazes of medieval specimens (both good and bad finishes) and in modern reproductions.

We have used the microEXAFS facility on beamline 10.3.2 at the Advanced Light Source to probe the local chemical structure of the copper in the lustre layers. Resolutions of 20μm were used to probe different locations within complex decorated specimens.

History

Originating from Iraq in about the 9th century AD, Islamic influences led to lustre production occurring in the Iberian peninsula from the 10th century onwards. Following the Christian occupation of Valencia in the 13th century, lustre production extends to the rest of Europe.

The craft

An initial, tin opacified, lead glaze layer is applied to the entire pot and then fired. This gives the background colour to the decoration. The lustre pattern is then painted on and the pot subjected to a second firing. Surplus lustre material is then removed to reveal the metallic decorative finish.

Production chemistry

Raw material for the underlying lead glaze, found at the site of a 13th century lustreware workshop in Paterna (Valencia), has been found to contain potassium whereas that used at the same time for non-lustreware does not. It is thought that the potassium in the glaze interacts with the copper in the applied lustre coating via a process of ion exchange to draw the copper into the glaze layer.

The lustre raw material contains a mix of clay, cinnabar (HgS) and copper and silver compounds – mostly oxides. The role of the cinnabar is believed to provide a locally reducing environment to convert the copper to a metallic state. The metal is known to form as nanoparticles in the glaze.

The samples

Two medieval pieces (M7 & M8) from the Paterna workshop and a series of 4 reproduction pieces (A1–4) have been investigated. The latter samples came from a traditional kiln belonging to a modern ceramicist working in a traditional manner. These four specimens were taken from different times in the second firing process at 500–550ºC.

Conclusions

Original lustreware from the Paterna workshop is obtained by complete reduction to copper metal. This is replicated in modern reproduction of the production technique.

The process of reduction is complex and in the early stages give a variety of copper phases which cannot be matched to combinations of pure metal and simple oxides.

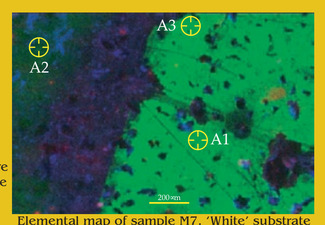
The presence of silver locally blocks reduction of the copper.

EXAFS amplitudes in copper and dark brown finishes of medieval and reproduction pieces are often suppressed, implying nanoclustering of the reduced copper without noticably affecting the visual appearance.

Medieval lustreware

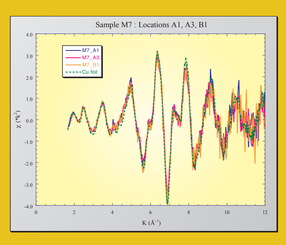
Cu K-edge EXAFS from the lustre coating (locations A1, A3, B1) in M7 show a good match to pure copper metal.

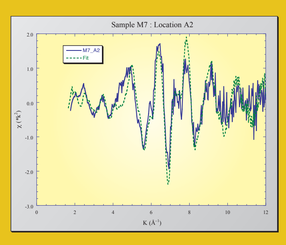
M7 (above) good lustre
M8 (below) poor lustre



Elemental map of sample M7. 'White' substrate on left, lustre finish on right. Green = copper, red= iron, blue = calcium.

Trace copper found in the white region (location A2) is in a combination of –approximately– 60% metal and 40% oxide (Cu_2O), indicating imperfect reduction of the copper here.





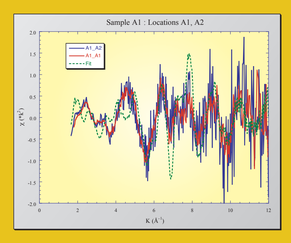
EXAFS from the lustre decoration on the second Paterna specimen (M8) is also fitted by the metal phase, but at a reduced amplitude varying between 70 & 90% depending on location.

Reproduction lustreware

A1

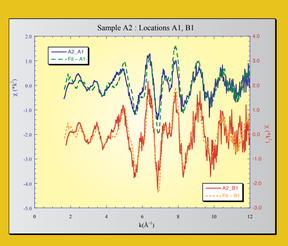
This does not exhibit any visual indication of lustre finish, being essentially the same colour as the underlying glaze.

Copper concentration in the glaze is low and the EXAFS is only poorly fitted by a mix of Cu, Cu_2O and CuO (40%/40%/20%), indicating the presence of other copper phases.

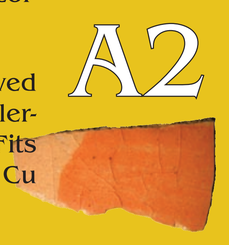


A2

The lustre layer has acquired a red–brown colour.



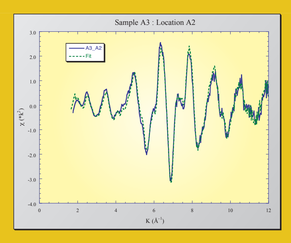
Some variation in copper phases is observed across the sample, EXAFS can be fitted tolerably well by combining Cu metal with Cu_2O. Fits shown are for 50% Cu (location A1) & 60% Cu (location B1), remainder Cu_2O.



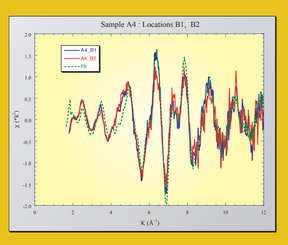
A3

The lustre layer has a metallic finish.

The Cu EXAFS can be fitted to Cu metal with a reduced amplitude of 80%. The presence of any oxide phase can no longer be confirmed.



A4



Fully fired. The lustre layer has a deep metallic shine.

Again the Cu EXAFS can be fitted to pure metal, however for this sample an amplitude reduction of 50% is required, consistent with nanoclustering of the copper.

Silver in the lustre

Silver was also added to the lustre material and gave a more golden colour to the finished product. It tends to collect in grains up to a few hundred micron in diameter. It is also more easily reduced than copper.

A high silver region with low copper content was found in sample A3. An EXAFS fit of Cu and Cu_2O (20%/30%) is poor, implying the presence of other copper phases.

Visible microscope image and elemental maps of sample A3. Iron = red, copper = green, silver & potassium = blue.